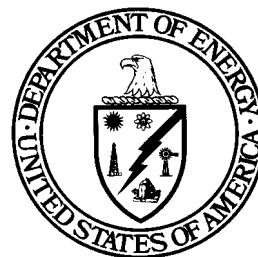


Stabilize High Salt Content Waste Using Sol Gel Process

Mixed Waste Focus Area



Prepared for
U.S. Department of Energy
Office of Environmental Management
Office of Science and Technology

September 1999

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OST Reference #2036

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Demonstrated at
Pacific Northwest National Laboratory
Richland, Washington

Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://OST.em.doe.gov> under "Publications."

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SECTION 1

SUMMARY

Technology Summary

Mixed waste sludges, soils, and homogeneous solids containing high levels of salt (~ greater than 15% by weight) have proven to be difficult to stabilize due to the soluble nature of the salts. The current stabilization technique for high salt waste, grouting with Portland cement, is limited to low waste loadings. The presence of salts interfere with the hydration and curing of the cement, cause waste form deteriorating mineral expansions, or result in an undesirable separate phase altogether. Improved technologies for the stabilization of salt waste must be able to accommodate higher salt loadings, while maintaining structural integrity, chemical durability, and leach resistance. In a joint collaboration supported by the Department of Energy's (DOE's) Mixed Waste Focus Area (MWFA), the Pacific Northwest National Laboratory (PNNL) and the Arizona Materials Laboratory (AML) at the University of Arizona have developed a sol-gel (wet-chemical) based, low-temperature-processing route for the stabilization of salt-containing mixed wastes. By blending and reacting liquid precursors at room temperature with salt waste, strong, impermeable "polyceram" matrices have been formed that encapsulate the environmentally hazardous waste components.

As depicted by Figure 1, polycerams are hybrid organic/inorganic materials with unique properties derived from the chemical combination of polymer (organic) and ceramic (inorganic) components. For this application, the stabilizing polyceram matrices contain polybutadiene-based polymer components and silicon dioxide (SiO_2) as the inorganic component. Polybutadiene (PBD) is a strong, tough, water-resistant plastic and its use in the polyceram promotes these same characteristics in the waste form. The PBD polymer component is modified to increase its reactivity with the SiO_2 precursor during sol-gel processing. When combined, the polymer and SiO_2 precursors react, gel, solidify, and encapsulate the salt waste components. The toxicity characterization leaching procedure (TCLP), Compressive Strength (ASTM C 39-94) and leachability tests (ANSI/ANS 16.1) confirm the efficacy of this approach, indicating that polyceram-based salt waste forms have the potential to provide end users with unique capabilities for disposing of salt-containing mixed wastes.

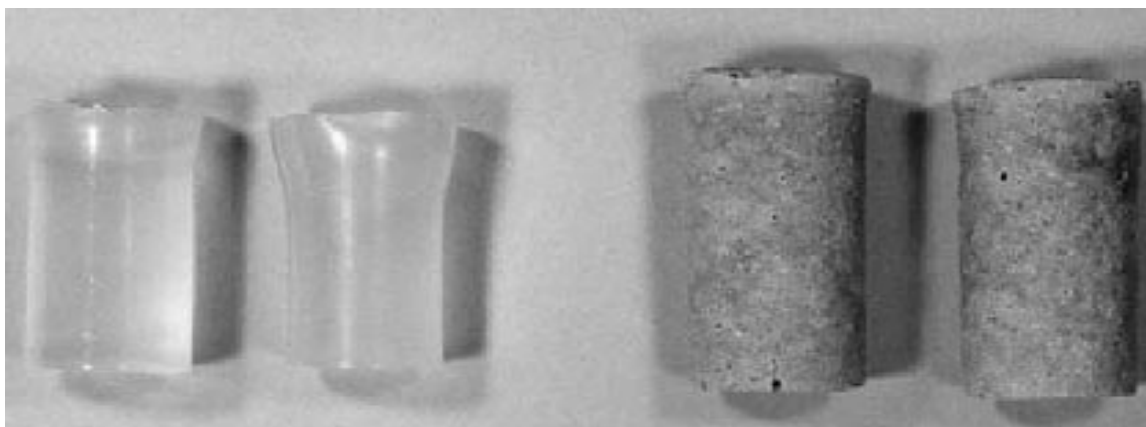


Figure 1. The cylinders on the left are polybutadiene-based polycerams. On the right are polycerams loaded with a 60-wt% salt-containing mixed waste surrogate.

Demonstration Summary

In order to demonstrate the effectiveness of the polyceram approach, several samples of different compositions were fabricated and tested against the preliminary criteria. The samples encapsulated salt waste surrogates with compositions recommended by the MWFA. Final waste form requirements provided by the MWFA specified the following criteria:



- Acceptable salt waste forms must possess an unconfined compressive strength of at least 60 psi (measured using ASTM C39-94)
- Leaching behavior characterized by the ability to meet Resource Conservation and Recovery Act (RCRA) Land Disposal Requirement standards as determined by the TCLP.
- Leachability Index (LI) of at least 6.0 for the salt components as measured using ANSI/ANS 16.1.
- Forms must also incorporate at least 10-wt% of the salt component in the final waste form.

Using simple sol-gel techniques, laboratory-scale salt waste forms incorporating two different salt waste surrogates at waste loadings of 50 to 70% were fabricated. One surrogate contained appreciable nitrate salts and the other contained both chloride and sulfate salts. The compositions of the waste surrogates that were established by the MWFA are representative of much of the salt waste present throughout the DOE complex. The salt waste surrogate was mixed into the precursor solution and the slurry was cast into molds after which it gelled. After drying, the samples were then subjected to various tests as required by the MWFA. The first generation of samples were much stronger than the requirement of 60 psi for mechanical strength and exceeded the ANSI/ANS 16.1 LI requirement of a minimum value of 6.0. However, they contained open porosity, which exacerbated chemical leaching, resulting in unfavorable TCLP test results. After modifying the processing procedure to eliminate open porosity, the polyceram waste forms containing 50% of the chloride/sulfate salt surrogate met all TCLP requirements at the higher non-Universal Treatment Standards (UTS) levels. Because of their increased densities, it is anticipated that these final waste forms are stronger and possess higher leachability indices than the first generation samples. Work is continuing to confirm this expectation.

To summarize:

- Polyceram salt waste forms have been fabricated using a simple, low-temperature, sol-gel process route.
- A wide range of waste types and loadings can be accommodated in these waste forms while maintaining mechanical integrity.
- Polyceram encapsulation prevents leaching of RCRA toxic metal components.
- Leaching of salt ions is reduced to low levels.
- Polyceram waste forms provide an easy and flexible means to dispose of salt-containing mixed wastes.

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SECTION 2

TECHNOLOGY DESCRIPTION

Overall Process Schematic

Standard sol-gel techniques were used to prepare the polyceram precursor solutions. The ceramic portion was formed after Tetraethylorthosilicate (TEOS) was prehydrolyzed with acidified H₂O (0.15M HCl) in tetrahydrofuran (THF). The side-modified polybutadiene was added and the solution was refluxed for 30 minutes. While mechanically stirring the solution at room temperature, salt waste surrogate was mixed into the solution. Stirring continued until the solution thickened. The solution was transferred into a plastic container, allowed to gel, and capped (the cap was punctured with small holes to allow gas to escape). After gelling, the gel in the capped container was dried in an oven at 66°C for a minimum of 24 hours. Finally, the samples were placed into a vacuum oven at 70°C for 3 hours. This procedure is shown in Figure 2.

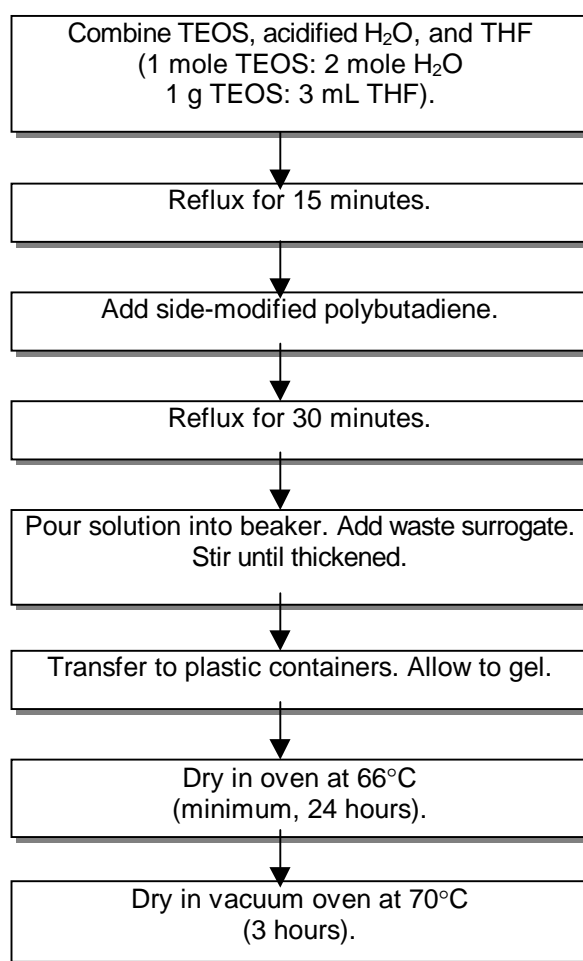


Figure 2. Synthesis procedure for polyceram waste forms.

After initial testing, it was apparent that the presence of open porosity in the samples was seriously affecting leach resistance. In order to minimize open porosity, the dried samples were submerged in either a polyceram or a resin solution and placed under vacuum to allow infiltration and filling of the pores. After infiltration, the samples were dried in an oven overnight. The samples receiving the additional processing step demonstrated greatly improved leach resistance. Work continues to develop other techniques by which open porosity may be minimized in these samples to further improve performance.

System Operation

Sol-gel processing is a general synthesis technique by which liquids are controllably reacted to produce solid matrices, such as the polycerams developed specifically for the salt waste in this study. The solid matrices form as a result of the creation of a network of covalent bonds at a low temperature. The two basic and generic sol-gel reactions used to produce the solid network are indicated below:



The most frequently used chemicals in sol-gel processing are silicon alkoxides. Silicon alkoxides are metal organic compounds that consist of a silicon atom bonded to at least one alkoxy groups (OR). When exposed to water, as in the hydrolysis reaction, the alkoxy group is replaced by the hydroxyl group (OH). This primes the molecules for condensation. During the condensation reaction, two $\equiv\text{Si-OH}$ molecules react to form the metal - oxygen - metal bonding required for network creation. As these reactions proceed at room temperature, the liquid gels. When solvent (ROH) is removed by drying, a hard solid network is formed. If only silicon alkoxides are used, the final product consists of a porous, amorphous silica, which, when fired at about 900°C, densifies and forms silica glass. Since low-temperature methods are desired for the salt containing mixed waste the firing step can be omitted. This omission of firing is acceptable for the polycerams as indicated by the lack of a firing step in Figure 2. Alkoxides and salts of metal cations other than silica can be used in the sol-gel process to make multicomponent oxide materials as well

Many processing advantages are associated with the use of sol-gel techniques to synthesize oxides (ceramics). Since oxide network formation occurs in the liquid state, where atomic level mixing is easily achieved, materials with excellent chemical homogeneity or controlled levels of homogeneity can be fabricated at temperatures, which, in many cases, are at or near room temperature. Also, composition modifications are easily implemented by merely changing the relative amounts of different metal alkoxides. Since network formation occurs at temperatures that are much lower than those required for facile molecular diffusion in the solid state, nonequilibrium and novel phases and microstructures can be generated in solution derived materials. For example, almost all sol gel-derived materials are amorphous when first fabricated, regardless of composition. In many cases, the conversion of this amorphous structure into crystalline phases can be directed through a variety of desirable metastable phases and phase assemblages. Finally, sol-gel technology has a demonstrated capability to generate gels and solids that encapsulate or incorporate large volume fractions of second phases. This advantage has obvious implications for the current salt-containing waste stabilization application.

Of particular note is the ability to fabricate a new class of materials, called "polycerams," by sol-gel processing. Polycerams are materials with network structures that combine carbon or silicon based organic polymers with oxide based ceramics, thus the name POLYmer + CERAMic \Rightarrow POLYCERAM. In most polycerams, the linkage between polymer and oxide components is usually made through siloxane (Si-O-Si) bonds. Polymers are flexible, deformable, tough, somewhat permeable to water, and can be processed using low temperatures. Ceramics are hard, strong, radiation resistant, leach resistant, and water impermeable, but require high temperatures to process. The properties of polycerams, which result from the chemical combination of polymers and ceramics, lie between those of the end member materials.

Salt waste forms were synthesized using polybutadiene-based polyceram matrices. Polybutadiene (PBD) was selected for the polymer component of the polyceram matrix because it is very strong, durable, and tough. It is largely impermeable to water, being the basis of most rubbers, and has good chemical



durability. The particular PBD precursor utilized was a side-modified (SM) functionalized PBD molecule (SMPBD). In this molecule, side groups are attached along the polymer chain, which contain siloxane-linking groups of triethoxysilane. The ceramic component in the polycerams is SiO_2 and is derived from the precursor tetraethyl orthosilicate (TEOS). Figure 3 is a schematic drawing showing the chemical combination of SMPBD and TEOS, forming a siloxane bond between the components. These bonds provide crosslinks between the polymer and ceramic components and establish the polyceramic matrix. The salt waste is encapsulated in the polyceramic matrix and stabilized.

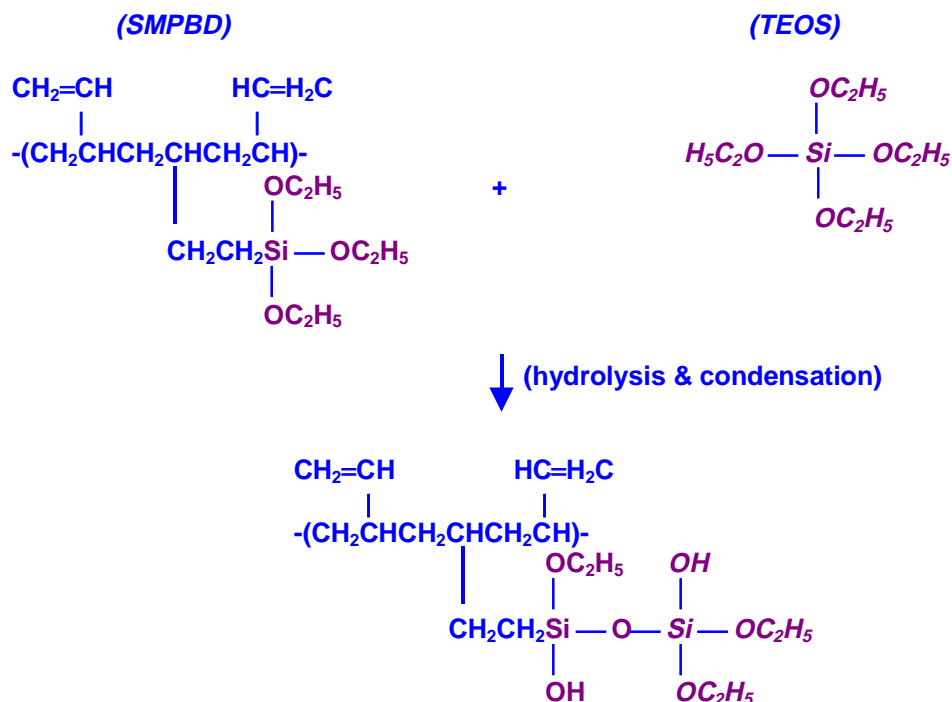


Figure 3. Schematic of siloxane bond between polymer component (SMPBD) and ceramic component (TEOS).

SECTION 3

PERFORMANCE

Demonstration Plan

To provide a uniform basis for comparison, the MWFA designed two salt-containing, nonradioactive, mixed waste surrogates for testing purposes. One of the surrogates represents the majority of previously grouted dry solids in the complex and contains a high level of nitrates. The other surrogate waste contains both chlorides and sulfates and represents an unconcentrated blowdown from an incinerator or thermal unit. The actual chloride-based surrogate prepared for testing contained ~ 19 -wt% salt (with NaCl and CaSO₄ as the major components) whereas the nitrate-based surrogate contained ~ 62- wt% salt (with NaNO₃ as the major component). Both salt waste surrogates contained 1,000 mg/kg each of the toxic metal oxides PbO, CrO₃, HgO, CdO, and NiO. The compositions of the original two surrogate recipes as recommended by the MWFA are shown in Table 1. The difference between the recommended and actual salt concentrations in the surrogates was a result of acceptable errors in surrogate formulation and mixing. Various quantities of these surrogates were incorporated into polyceram matrices to generate final waste forms for testing.

Table 1. MWFA salt waste surrogates.

Constituent	High Chloride Weight Percent (wt%)	High Nitrate Weight Percent (wt%)
Fe(OH) ₃	12.75	6.0
Al ₂ (OH) ₃	8.5	4.0
H ₂ O	29.75	14.0
Mg(OH) ₂	8.5	4.0
Micro-Cel E	17.0	8.0
Portland Cement (Type II)	4.25	2.0
Na ₂ PO ₄	4.25	2.0
NaCl	10.0	0.0
CaSO ₄	5.0	0.0
NaNO ₃	0.0	60.0
Toxic Metal Oxides	(mg/kg)	(mg/kg)
PbO	1,000	1,000
CrO ₃	1,000	1,000
HgO	1,000	1,000
CdO	1,000	1,000
NiO	1,000	1,000
Hazardous Organic	(mg/kg)	(mg/kg)
Trichloroethylene	1,000	1,000

Of particular concern in the design of a synthesis route for sol gel-derived waste forms is the desire to achieve high density (low porosity) in the polyceram matrix. This will enhance mechanical strength, water impermeability and leach resistance. In other polyceram systems (Suratwala et al.1997), such as the polydimethyl-siloxane (PDMS) - SiO₂ system, the ratio of PDMS/SiO₂ (organic to inorganic) played a key role in establishing whether or not the polyceram became fully dense during processing or developed a pore structure containing very small pores and extremely high surface areas - in the range of 100s of m²/gm. Based on this experience, test samples were produced that contained five different polymer-to-ceramic ratios.

The amount of waste loading will also play a critical role in establishing full density. Studies from glass/ceramic composites show that the physical distribution of the second phase (in our case - the salt waste) may play an important role in allowing the host matrix to densify during further processing. If the second phase forms an interconnected structure, then only about 15% can be added and still achieve full



density. If the second phase particles are isolated - one from another - then significantly higher loadings can be achieved. Consequently, a range of waste loadings of both the chloride-based and nitrate-based salt waste surrogates were studied to maximize waste loading and to establish the sensitivity of properties to variations in composition. Table 2 is a sample matrix that shows the ranges of SMPBD polymer-to-TEOS ratio and waste loadings that were investigated. The checkmarks in Table 2 indicate those samples that were prepared and tested in this study.

Table 2. Sample matrix.

Polymer:TEOS (wt%)		25:75	36:64	50:50	62:38	75:25
Chloride-based Surrogate Waste Loading (wt%)	50	√	√	√		
	60		√	√	√	√
	70	√	√	√		√
Nitrate-based Surrogate Waste Loading (wt%)	30	√	√			
	40			√		√
	70		√			

Sample ID	Polymer:TEOS Ratio (wt%)	Polymer:Silica Ratio (wt%)	Waste Loading (wt%)	Salt Content- Chloride Based Surrogate (wt%)	Salt Content- Nitrate Based Surrogate (wt%)
36C50	36:64	66:34	50	9.625	
36C60	36:64	66:34	60	11.55	
36C70	36:64	66:34	70	13.475	
50C50	50:50	78:22	50	9.625	
50C60	50:50	78:22	60	11.55	
50C70B	50:50	78:22	70	13.475	
62C50	62:38	85:15	50	9.625	
62C60	62:38	85:15	60	11.55	
75C60	75:25	91:9	60	11.55	
36N30	36:64	66:34	30		18.6
36N70	36:64	66:34	70		43.4
75N40	75:25	91:9	40		24.8

Measurement of Compressive Strength

The compressive strength of the polyceram salt waste forms was measured using as-prepared polyceram cylinders (two each). The test method used to determine compressive strength was ASTM C 39-94. Per ASTM C 39-94, the preferred test specimen is a monolithic cylinder with a length to diameter ratio (l/d): $1.8 < l/d < 2.2$. Samples tested had a length to diameter ratio equal to approximately 2, (1.5 in. length and 0.75 in. diameter). Per requirements, the mean compressive strength of representative samples must be equal to or greater than 60 psi. Duplicate samples for each polyceram waste form were tested.

The as-prepared polyceram cylinders were trimmed to a height of 1.5-in. using a diamond saw to achieve a more consistent load over the cylinder surfaces. The cylinders were then capped on both ends using Hydro-Stone Gypsum Cement capping compound.

The equipment used in the compression test consisted of a Cal-Tek Compression Machine, Model No. Ct-400K-2R Omega/Revere and Total Comp. load cell. ELE Dial indicator, Model No. LC-2, and calipers, Strata No. G00172.



Results

The results of compressive strength testing as per ASTM C 39-94 are shown in Table 3. In all cases, the mechanical strength of the waste forms exceeded the minimum requirement of 60 psi. The actual strengths ranged from an average of 150 psi to over 1,500 psi.

Table 3. Compressive strength testing results.

Sample ID	Compressive Strength at Which Polyceram Cylinders Broke		
	Cylinder 1 (psi)	Cylinder 2 (psi)	Mean (psi)
36C50	1,053	1,125	1,089
36C60	923	1,177	1,050
36C70	743	788	765
50C50	273	308	290
50C60	204	425	314
50C70B	589	539	564
62C50	126	148	137
62C60	182	127	154
75C60	204	94	149
36N30	1,087	569	828
36N70	1,485	1,542	1,513

Measurement of Leachability Index, ANSI/ANS 16.1

Unlike the one-time TCLP RCRA required leach tests, the ANSI/ANS 16.1 test defines a particular component's or element's leaching behavior from a waste form over a period of time (e.g. 90 days, 5 days). This behavior is quantitatively reported as the Leachability Index, (LI). In theory, LI is the negative value of the exponent of the component's diffusivity constant. This constant is unique for each element in a given environment and its value depends on the temperature and properties of the leaching medium or fluid (e.g. water). By definition the diffusivity is a proportionality constant that relates the element's concentration gradient (i.e. the difference in element concentration between the waste form and that of the leaching fluid) to the rate of element leaching from a unit cross-section of waste form. Therefore the less an element leaches, the lower is its diffusivity and the higher its Leachability Index, or LI. The NRC has established the requirement that waste forms destined for disposal in NRC licensed facilities must have LI's of 6 or greater for specific components and elements. Even though DOE mixed waste forms do not require these tests for disposal in a non NRC site, ANSI-ANS 16.1 is an excellent method for obtaining additional waste form leaching performance and durability data at the development stage.

The disposal criteria established for salt waste forms does not indicate which elements must possess an LI in excess of 6. Because of recent emphasis on the potential impact of chloride- and nitrate-based salt contaminants on biologically active environments, the leachability indices for the chloride (Cl^-) and nitrate (NO_3^-) ions were measured for the polyceram waste forms.

Cylinders of 15 polyceram salt waste forms were produced for either chloride or nitrate leachability testing using the ANSI/ANS 16.1 methodology. Polyceram salt waste form cylinders with dimensions of approximately 0.75-in. diameter and 1.5 in. height were produced by pouring the polyceram-salt waste mixture into plastic molds before solidification and then allowing them to dry. Per ANSI/ANS 16.1, the preferred test specimen is a monolithic right circular cylinder with a length-to-diameter ratio in the range of 0.2 to 5.0). All samples had a length to diameter ratio equal to 2.

ANSI/ANS 16.1 testing procedures were used to determine either the chloride or nitrate short-time "abbreviated test" LI over a 5-day test period. The full ANSI/ANS 16.1 testing procedure requires that the leachant volume be sampled for testing and completely replaced at 11 designated intervals.



Throughout the test, the leachant volume was maintained at a required level such that the ratio of the leachant volume, to cylinder surface area, equaled 10 ± 0.2 cm.

The ANSI/ANS 16.1 test vessels were Nalgene 250-mL bottles with certified I 300 series labels. Deionized water was taken from a Barnstead, Nanopure II water purifier.

Results

Table 4 lists the LI values obtained for the polyceram salt waste forms, using the ANSI/ANS 16.1 short-time “abbreviated test,” as well as the concentrations of chlorine and nitrate in the samples. All of the chloride or nitrate LI values are above the LI minimum limit of 6.0.

Table 4. Leachability Index values of polyceram cylinders.

Sample ID	Chlorine Ion wt%	Nitrate Ion wt%	Leachability Index
36C50	3.03		8.5
36C60	3.64		7.5
36C70	4.25		7.6
50C50	3.03		8.1
50C60	3.64		7.8
50C70A	4.25		8.2
50C70B	4.25		8.2
62C50	3.03		8.2
62C60	3.64		8.2
75C60	3.64		7.9
75C70	4.25		7.6
36N30		13.13	7.1
36N70		30.64	7.6
50N30		13.13	8.4
50N40		17.51	7.9

Measurement of Leachability Using the Toxicity Characterization Leaching Procedure (TCLP)

For TCLP testing, approximately 10 g of solid material (cubed polyceram < 1 cm) were leached with 0.2 liters of either TCLP extraction fluid #1 (acetic acid and sodium hydroxide solution @ pH = 4.88) or extraction fluid #2 [acetic acid and ASTM Type II water (deionized water) @ pH = 2.85]. The RCRA defined protocol for the TCLP test method requires that 1 of 2 leaching solutions be used depending on the pH of the waste form. Waste forms with pH below 5 require use of extraction fluid #1, whereas those with pH above 5 require use of extraction fluid #2. This requirement attempts to ensure that a basic waste form does not appreciably neutralize the leaching solution, thereby limiting its ability to extract hazardous constituents from the waste form. Polyceram samples 50C70A, 75N40, 50N40, 50N30, 50C60, 75C60, 36C60, 36N30, 36N70, 62C60, 62C50, 50C50, 50C70B, and 36C50 required use of extraction fluid #1 and polyceram samples 25C70, 75C70, and 36C70 required use of extraction fluid #2. Samples were leached for 18 h before being filtered. After filtration, the leach solution pH was approximately 4.35 to 5.0. Following the leach procedure, 10-mL aliquots of each sample were prepared for mercury analysis using a digestion, cold vapor atomic adsorption (CVAA) procedure. Each leachate solution was prepared for ICP-AES (inductive coupled plasma-atomic emission spectroscopy) analysis by digesting 100-mL aliquots in open beakers using HNO₃ and HCl acid according to the SW846 - Method 3010A procedure.

The TCLP test, per the Environmental Protection Agency (EPA) SW-846, Method 1311, was conducted to determine if the polyceram waste forms would still have a RCRA hazardous waste designation. Particle size reduction was required so that the polyceram particles were capable of passing through a 9.5-mm (0.375-in.) standard sieve. The reduced polyceram samples, approximately 10-g, were placed



into an extractor vessel with an extraction fluid equal to 20 times the weight of the polyceram sample. The sample was rotated at 30 rpm for 18 hours at room temperature. The liquid was separated from the solid phase by filtration, and the leachate was analyzed for RCRA metals (i.e., As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) via Inductive Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES) or CVAA.

Results

The salt waste surrogates contain the RCRA metals Pb, Cr, Hg, Cd, and Ni. TCLP testing indicated that the first generation of samples, which contained extensive open porosity, did not meet RCRA Land Disposal Requirements for several of the metals. In particular, while the concentrations detected for Pb were well within acceptable levels, the results for cadmium, chromium, and mercury were two to five times that which is allowed by regulation. Analyses to determine compositional variations in leaching behavior were inconclusive, supporting the idea that open porosity dominated the leach resistance behavior of these first generation polyceram waste forms.

In order to improve leach resistance, additional samples were prepared and infiltrated with either polyceram solution or a resin solution after the drying step. The infiltration was performed under vacuum, allowing the solution to fully penetrate and fill open pores. After infiltration, the samples were dried in an oven at 66°C overnight. Continued development is required to validate this method at production scales. As seen in Table 5, this additional processing step produces samples that meet the RCRA Land Disposal Requirements for toxic metals. Coupled with the results for compressive strength and LI, the TCLP data from these samples confirm that polybutadiene-based polycerams successfully encapsulate salt wastes as per the criteria established. Currently, work is underway to eliminate the need for the additional infiltration step. Emphasis is being placed on minimizing open porosity in the polyceram matrix after the initial drying step. This improvement should be readily achieved by reductions in the cross-link density of the polyceram matrix.

As the next generation of Land Disposal Requirements may require that the Universal Treatment Standards (UTS) level limits be met for hazardous constituents (per 40 CFR-Protection of Environment, Section 268.48 Universal Treatment Standards), they are a good benchmark for waste form performance. The UTS limits for the hazardous metals contained in the salt waste surrogates are also listed in Table 5. Again, using the same TCLP testing methodology, samples 50C50-IPC and 50C50-IR exhibit hazardous metal releases that are very near or below the UTS limits. Nickel release was measured for both the 50C50-IPC and 50C50-IR samples using the TCLP testing methodology. The nickel releases were both below the detection limit, which was 0.030 µg/mL.

Table 5. TCLP Inorganic results for infiltrated polyceram salt waste forms.*

Analyte:	TCLP Limit (µg/mL)	UTS Limit (µg/mL)	50C50-IPC (µg/mL)	50C50-IR (µg/mL)
Arsenic	5.0	5.0	---	---
Barium	100	7.6	---	---
Cadmium	1.0	0.19	[0.24]	[0.13]
Chromium	5.0	0.86	[0.99]	[0.14]
Lead	5.0	0.37	---	[0.07]
Mercury	0.2	0.25	[0.23]	[0.044]
Selenium	1.0	0.16	---	---
Silver	5.0	0.3	---	---
Nickel	na	5.0	---	---

a. Results in brackets are above the instrument detection limit, but below the practical quantification limit. "----" Indicate measurement is below detection. "na" is not applicable. "nm" is not measured. As, Ba, Cd, Cr, Pb, Se, and Ag leachate metals analysis results via ICP-AES. Hg metal analysis result via CVAA.

Summary



Table 6 combines the test results for a subset of the tested samples. Samples 36C50, 36C70, 50C70, 36N30, and 36N70 exhibit excellent strength and LI, but their chemical durability is low because of the presence of open porosity. After undergoing the additional infiltration step, samples 50C50-IPC and 50C50-IR exhibit greatly improved chemical durability. Sample 50C50-IR passes the TCLP requirements for all toxic metals and sample 50C50-IPC passes the requirements for all but Hg, which had a level of 0.23 $\mu\text{g/mL}$, which is 0.03 $\mu\text{g/mL}$ above the limit of 0.2 $\mu\text{g/mL}$. Sample 50C50-IR passes the UTS requirements for all of the hazardous metals contained in the waste surrogate (Cd, Cr, Pb, Hg, and Ni). Sample 50C50-IPC passes the UTS requirements for all but Cd and Cr, which have a level of 0.24 $\mu\text{g/mL}$ (0.05 $\mu\text{g/mL}$ above the UTS limit of 0.19 $\mu\text{g/mL}$) and 0.99 $\mu\text{g/mL}$ (0.04 $\mu\text{g/mL}$ above the UTS limit of 0.86 $\mu\text{g/mL}$), respectively. Since the infiltration step increases the densities of the samples, it is anticipated that the compressive strengths and ANSI 16.1 leachability indices for 50C50-IPC and 50C50-IR will exceed those measured in Table 6 for waste forms with comparable compositions. Also, the data suggest that all of the samples in Table 6 would pass TCLP testing if they were given the additional infiltration processing step.

In summary, these results show that polyceramic waste forms meet the requirements established at the onset of the development program and can be fabricated using simple, low-temperature, sol-gel processes. These waste forms can accommodate a wide range of waste types and loadings while maintaining mechanical integrity. Also, the polyceramic matrix successfully encapsulates the salt waste, preventing the leaching of toxic metals, and reducing the leaching of salt ions to levels that are anticipated to be acceptable for long-term waste storage.

Table 6. Polyceramic waste form test results.

Sample ID	Salt Loading (wt%)	Chemical Durability-RCRA (TCLP)	Compressive Strength, psi (ASTM C 39-94)	Leachability Index (ANSI/ANS 16.1)
36C50	9.63	Did not pass	1,089.00	8.5
36C70	13.48	Did not pass	765.33	7.6
50C70	13.48	Did not pass	564.17	8.2
36N30	18.6	Did not pass	827.91	7.1
36N70	43.4	Did not pass	1,513.49	7.6
50C50-IPC ^a	9.63	Passed for Cd, Cr, Pb, and Ni	-	-
50C50-IR ^b	9.63	Passed for Cd, Cr, Pb, Ni, and Hg	-	-

a. Sample received a secondary infiltration of polyceramic solution after initial oven drying. As a result, the wt% waste and salt loading values are slightly less than the indicated values.

b. Sample received a secondary infiltration of resin solution after initial oven drying. As a result, the wt% waste and salt loading values are slightly less than the indicated values.



SECTION 4

TECHNOLOGY APPLICABILITY ALTERNATIVES

Competing Technologies

Over the last 50 years of DOE operations, large quantities of mixed low-level wastes (MLLW) were generated from past nuclear weapons based industries and more recently from waste treatment processes. Stabilization has been and still is an effective, inexpensive, and simple treatment alternative for many types of these mixed wastes. This alternative is also accepted as safe and environmentally sound by both the regulators and the concerned public. A review of the technical literature and of past DOE operating experience shows that low-temperature hydraulic cement, polymer, bitumen, and ceramic grout based stabilization methods produce waste forms that meet or exceed final disposal requirements [(Kalb et al. 1997) (Moghissi, Godbee, and Hobart 1986)]. The success level of the waste form is dependent on the original waste medium and the type and amount of hazardous and/or troublesome components in the untreated waste. Unfortunately, these current stabilization techniques have had limited success in accommodating homogeneous solid and sludge wastes containing relatively high concentrations of salts (EPA 1996) in addition to RCRA hazardous heavy metals.

Salts (defined as the reaction product generated when a metal ion replaces the hydrogen ion of an acid) are highly soluble, easily hydrated, and reactive. As a consequence of these characteristics, low-temperature stabilized forms of MLLW containing salts do not adequately cure or are susceptible to deterioration over time due to the expansion from the water-salt reaction. Salts interfere with the basic hydration reactions of cements and easily undergo dehydration/hydration cycles that can cause deteriorating expansions. This deterioration may lower the durability and strength of the stabilized waste form and create pathways for the hazardous and radiological constituents to be released from the immobilized waste.

In some cases, leach resistant salt waste forms of sufficient durability are possible with the current stabilization techniques. However, these techniques usually result in forms with excessive increases in waste volume due to low waste loadings. Basic Portland cement formulations can only accommodate ~15 wt% of salts. These process inefficiencies and subsequent high disposal costs offset any benefits. The limitations of these current methods are of immediate concern since future volumes of salt wastes are anticipated as other MLLW treatment processes are implemented. Future effluents from MLLW wastewater treatment systems and scrubber blowdown from future and present MLLW thermal systems (i.e., incinerators and melters) will significantly add to the MLLW salt inventory.

There are many mixed waste stabilization/solidification technologies at various stages of development that could be considered as competing with the sol-gel process. Numerous tests with low-temperature stabilization techniques involving ceramics and polymers indicate that greater waste loadings (than those achievable with conventional Portland cement) are possible with even the troublesome salt-containing wastes. In addition, alternatives involving thermal-sintering techniques also may lead to acceptable waste forms with considerably more volume reduction compared to that achievable with grouts or sol gel. Mixed waste stabilization methods currently in the later stages of development include phosphate-bonded ceramics, enhanced concretes using proprietary additives, and several methods provided by commercial vendors. Low-temperature methods like phosphate bonded ceramics not only provide a low porosity ceramic barrier, but render the RCRA metal less hazardous by converting it to the low solubility phosphate salt. Microencapsulation techniques involving polyesters, polyethylene, and polysiloxane have been demonstrated on surrogate and/or actual wastes.

Sintering differs from vitrification in that only melting at grain phase boundaries occur without the complete amorphous restructuring that takes place in glass formation. Like vitrification, sintering occurs at temperatures over 1,000°C and can emit volatile hazardous metals. Even though densification is possible for some additional volume reduction, slight volume increases usually occur. However, waste loadings as high as 80% are possible. The equipment for sintering is less complex than vitrification, but



more complex than grouting. For a typical sintering process, grinding, mixing, and extruding equipment are required as well as ovens, calciners, and offgas treatment systems. For most waste streams, sintering methods will require an extensive process development effort involving statistically designed experiments.

Recently developed polymeric methods using batch mixers or extruder systems are currently available. Like sol gel, these low-temperature microencapsulation techniques do not chemically incorporate the waste, but create an impermeable barrier between the hazardous components in the waste and the environment. Waste loadings in these organic media are usually on the order of 50% for many troublesome wastes, such as incinerator fly ash or those containing appreciable salts. This value is nearly twice that achievable with conventional cement grout methods. The primary advantage of sol-gel generated polyceram waste forms over other low-temperature polymeric and inorganic methods is the high degree of mixing achievable among the encapsulating chemicals and the actual waste. Unlike most of the alternatives, the liquid chemicals inherently result in more thorough mixing during processing in comparison to solid or sludge based systems.

Technology Applicability

Salt Waste Stabilization

Polyceram waste forms were specifically developed for stabilizing salt wastes. Salt wastes are typically chloride, hydroxide, nitrate, and/or sulfate salts of sodium that have been contaminated with a combination of organic solvents, heavy metals, and/or transuranic (TRU) elements. These wastes were byproducts of primary nuclear processing involving acids and metal finishing and a total inventory of over 10,000 m³ exists throughout the DOE complex (Beital 1997). In addition, salt wastes will be generated as byproducts of other decontamination and dismantlement (D&D) activities such as incineration and vitrification.

Salt wastes are generated as sludge and solid effluents having a broad range of chemistry. Thus far, the development of polyceram matrices for salt stabilization has focused primarily on solid salt wastes. Polyceram matrices allow tremendous flexibility, and, with continued development involving slight modifications of their processing and chemistry, there is the possibility that a wide range of waste compositions and waste loadings can be accommodated. Currently, techniques are being developed to use sol gel-derived polycerams for stabilizing slurries and liquid wastes.

Applicability of Sol-Gel Technology Throughout the DOE Complex

From a broader perspective, sol-gel processing techniques offer potential solutions to many of the most pressing environmental restoration problems facing the DOE nuclear complex. In the past, the unique capabilities associated with sol-gel technology have been exploited in a broad range of applications, including the fabrication of microspheres of U, Th, and Pu oxides for fuel cells and the immobilization of nuclear waste in glassy matrices. Attractive aspects of sol-gel technology are the abilities to prepare ceramic powders with tailored particle sizes without generating grinding debris; glasses with novel compositions and properties that cannot be made by conventional means; ceramic bodies with novel microstructures and tailored distributions of phases, including porosity; chemically homogeneous glass precursors using firing temperatures much lower than conventionally derive materials; and gel structures that can immobilize waste components in preparation for disposal.

The unique capabilities of the sol-gel process stem from its ability to create oxide networks through chemical reactions at or near room temperatures. These networks can be used to encapsulate or incorporate other components such as waste species. Finally, the surrounding matrices can be retained in the gel state or can be densified at temperatures that are much lower than conventional firing temperatures. Reduced firing temperatures result from the high level of homogeneity that is present in the sol-gel matrix as a result of chemical mixing in the liquid state. In addition to the polyceram sol gel-derived materials, other sol gel- derived materials for application in waste remediation and removal can be categorized as follows:



- Silicate based oxide gels [(Zelinski and Uhlmann 1985) (Uhlmann 1992) Brinker and Scherer 1990)] - The chemistry of these gels is based on SiO₂, making them compatible with vitrification schemes for waste disposal.
- High solids-content gels (Rabinovich 1988) - These gels contain large concentrations of already condensed material, such as sludge particles that increase the mechanical integrity of the gel.
- Collapsible and reversible gels (Tanaka 1981) - Collapsible gels are gels whose volume can be drastically reduced (as by expulsion of the solvent phase) by slight variations in the environment. Reversible gels can be formed and dissolved repeatedly by modest changes in the chemical environment.
- Light element gels [(Tohge, Matsuda, and Minami 1987) (Irwin et al. 1987) (Haaland and Brinker 1984)] - Gels that contain light elements, such as boron, have the potential to aid in attenuating the neutron flux from waste materials.

Examples of potential applications for the use of the above sol-gel technologies within the DOE complex are discussed below (Zelinski 1998). It is important to note that these applications would require validation through additional and possibly extensive development activities.

Encapsulation of Spent Nuclear Fuel Elements

Corrosion and handling damage have reduced the mechanical strength of many reactor fuel element containers, which complicates handling and stabilization efforts because of the potential for leaks and spills. Sol-gel processing could be used to stabilize the corroded fuel elements by in-container encapsulation. Precursors could be added to the containers that, upon gelation, would surround, contain, and stabilize the fuel and waste components.

Stabilization of Fuel Basin Sludge

In some fuel cell storage basins, reaction products from the corrosion and disintegration of fuel elements and other debris have formed a sludge layer on the floor of the basins. Irradiated fuel may accumulate on the basin floors from fuel oxidation and fuel handling operations. In addition to the U and Zr oxides, aluminum oxide/hydroxide, iron oxide, concrete grit, lost tools, miscellaneous hardware, and other oxides and materials may be components of the basin sludge. Sludge stabilization via sol-gel processing is based on the use of wet chemical means to create a gel matrix in-basin, which will contain and stabilize the sludge components. In use, the gelling medium will be delivered to the sludge in-basin. Once the gel components have permeated the sludge volume, gelation will be induced, causing the sludge to be incorporated in a gel matrix.

D&D of Contaminated Pipe Networks

Facilities used in defense-related nuclear materials development often contain networks of contaminated piping that have been exposed to aqueous environments for long periods of time. In some cases the piping has corroded to the extent that its mechanical integrity is in question; and sectioning and removal of the pipe pose an increased risk of further contamination and airborne radioactivity.

The use of sol-gel processing for D&D pipe activities is based on the ability to form a solid gel from liquid precursors. This provides the potential to: (1) immobilize liquid and surface contaminants inside the pipes, (2) reduce the risk of further airborne contamination during pipe sectioning and removal, and (3) enhance the pipe mechanical strength for handling and transportation.



In Situ Barrier Formation Between Nuclear Facilities or Contamination and the Environment

The initial inherent fluidity of sol-gel systems and the ability to preprogram their gelation rate makes them excellent candidates for the production of engineered barriers to isolate environmental hazards. They can be injected into porous media (e.g., soil) that surround waste tanks, forming a second, independent containment barrier for aging waste tanks. Similarly, sol-gel systems can be used to stabilize trench wastes until final disposition can be accomplished; or such a treatment could provide a permanent solution.

Patents/Commercialization/Sponsor

Polyceram matrices for the encapsulation of salt waste have been developed via sponsorship of the MWFA through collaborative efforts between the PNNL and the AML, which is the research branch of the Materials Science and Engineering Department at the University of Arizona. This work is based on earlier collaborative efforts between PNNL and AML to develop sol-gel technologies to facilitate remediation, decommissioning, and disposal activities throughout the DOE complex. These efforts have resulted in an invention disclosure, the focus of which is the development of technology to form ceramic/glass precursor structures in and around waste components or contaminated processing components in the presence of large quantities of water (e.g., underwater).

Throughout the development of polyceram matrices for salt waste stabilization, the PNNL/AML team has had access to the technical and industrial expertise of the Donnelly Corporation. This corporation is an international automotive supplier dedicated to serving customers around the globe through the use of sol-gel technology and other innovative approaches to fabricate high-quality molded and coated glass products. The company has been based in Holland, Michigan, since 1905, and today operates from 25 locations in the U.S., Mexico, Europe, and Asia. Donnelly and the University of Arizona have an excellent working relationship through the AML and when sufficient end-user interest is generated for this technology, routes to commercialization of this technology will be jointly explored.



SECTION 5

COST

Cost Analysis

To date, no detailed cost analyses have been conducted on the use of polyceram matrices for salt waste stabilization. Some of the raw materials, in particular, the side-modified polybutadiene precursor, are specialty chemicals that are not currently manufactured in large volumes. After assessment of end-user interest and needs, estimates of chemical costs based on realistic production volumes can be obtained. With this information, reasonable estimates of the costs associated with this emerging technology can be developed.

One of the attractive features of sol-gel technology is that it involves simple processes such as mixing of chemicals, casting or extrusion, drying, and final packaging. As a result of these simple processes, it is anticipated that the scale-up of the fabrication route for polyceram salt waste forms will be relatively straightforward and involve the use of conventional, low capital chemical mixing tools, e.g., 55-gallon drums and standard drum mixers. Another attractive feature is that the polycerams have a high probability of containing higher salt-containing waste loadings in comparison to the baseline Portland cement grout technology. For many applications, this will result in considerable cost savings due to the lower net waste volumes requiring handling, shipping, and final disposal. Current estimates put these savings at ~ \$150 per drum of treated waste.

Based on the above assessments a ROM estimate for installation, start-up, and capitol costs is possible. Assuming a system similar to that currently used for low temperature cement and ceramic methods, design, capitol equipment, installation and start-up costs would range between \$600K to \$1000K. This estimates assumes an available facility for housing the equipment with a through put capacity of ~ one 55 gallon barrel per day. The cost estimate also includes those resources necessary to secure the required environmental and operating permits (~200K). These cost s are considerably less than those required for a comparable vitrification or high temperature system, where development, design, installation and capitol costs can exceed \$10,000K.



SECTION 6

REGULATORY AND POLICY ISSUES

Regulatory Considerations

The regulatory goal of any end user deploying the sol-gel process is to produce polyceramic encapsulated waste forms that meet Land Disposal Restrictions (LDRs) for land burial. In most applications, this means that the RCRA 40 CFR 268.40 treatment standards must be met at the lower limits proposed by the UTS, if the waste form is to be placed in a Subtitle D landfill. As a result, any full-scale, sol-gel treatment facility will require a Part B RCRA permit or a modification to an existing permit.

In addition, Nuclear Regulatory Commission (NRC) 10 CFR 61 waste form testing will be necessary if disposal is to be in an NRC licensed facility. Additional requirements for applying the sol-gel process at a federal facility include a National Environmental Policy Act (NEPA) review (a categorical exclusion is most likely to be applied), and any air emission considerations and/or permits as required under the National Environmental Standards for Hazardous Air Pollutants (NESHAPS). Any commercial facility treating radiological waste must secure an NRC permit.

If future development of the sol-gel process requires testing with actual waste streams, a NEPA approval through categorical treatability study exclusion must be obtained. The state cognizant environmental agency in which the treatability study is to be performed must be notified 45 days before receiving archived samples for testing. In addition, the regional EPA must be notified.

Safety, Risks, Benefits, and Community Reaction

Sol-gel encapsulation is an inherently safe, low-temperature operation not prone to fire, explosion, or excessive heat of upon gelation. The produced polyceramics are not chemically toxic or hazardous and the base liquid chemical precursors of TEOS and PBD do not require any special handling techniques outside of normal laboratory practices. Simple industrial equipment can be used to implement the technology and standard radiological controls can be applied to avoid the spread of contaminants during processing. Since there is no known offgassing of hazardous or radioactive materials, there are no airborne safety problems.

Community stakeholder reaction to the sol-gel treatment of mixed waste is anticipated to be favorable, since the process produces little secondary liquid waste and no offgas emissions. If the porosity problems are adequately addressed, the waste form will be perceived as having an equivalent durability to the baseline Portland cement process. In addition, higher waste loadings will reduce the volume requiring final disposal. Some negative stakeholder reactions could come from the state where final waste disposal is to occur, or from out of state if transportation issues exist. However, no adverse public or tribal input regarding the sol-gel technology has been received.



SECTION 7

LESSONS LEARNED

Technology Selection and Implementation Considerations

To be attractive to end users, emerging technologies for encapsulating salt wastes should be able to accommodate salt loadings in excess of 15% by weight of salt. Also, the new waste form must be able to accommodate a wide range of salt waste compositions, ranging in chemistry from nitrates to sulfates to chlorides, with variable types and concentrations of toxic metals and organic contaminants. The flowsheet for waste form fabrication should be simple, easy to implement, and safe. It should minimize the introduction of secondary wastes while maximizing operational flexibility. Finally, waste form fabrication must be cost-effective for the end user.

After a year of development work, sol gel-derived polycerams have emerged as a technology that shows significant potential for meeting these implementation criteria. In this technology, the matrix encapsulates the salt waste. Consequently, the waste components are not chemically incorporated into the waste form. This reduces chemical interactions that can degrade the performance characteristics of the matrix. As a result, the waste form can accommodate a wide range of waste compositions and loadings. Also, the matrix is based on a polymer, polybutadiene, which is impermeable to water. This reduces the degree to which water can penetrate into the waste form and minimizes the extent to which salt and other waste components can diffuse through the matrix.

The polyceram waste form is fabricated using simple processes, including the addition of chemicals, stirring, and drying at temperatures less than 100°C. At present, a second infiltration step is required to achieve optimal performance, but efforts are underway to modify the process to eliminate this step. This simple processing is possible because sol-gel reactions are being exploited to form the matrix around the waste components. These hydrolysis and condensation reactions proceed rapidly at room temperature to create the encapsulating matrix at or near room temperature. Because processing occurs at low temperatures, the losses of waste components through volatilization are kept to a minimum with no generation of significant quantities of secondary waste.

Technology Limitations and Needs for Future Development

Deployment of polyceram technology in the DOE complex would be facilitated greatly by additional developmental work. In particular, efforts should be directed to eliminate the secondary infiltration step. The chemistry of the PBD-based polyceram system lends itself to easy manipulation of the connectivity and rheological characteristics of the waste form. By appropriately adjusting the concentration and degree of modification of the side-modified polybutadiene polymer precursor, it should be possible to generate a matrix that can be densified at temperatures between 100 and 150°C. With this modification, the salt waste can be incorporated into the gel material, dried, and consolidated or extruded to form a monolith free of open porosity.

Also, the current formulations for the polyceram matrix include organic solvents. The removal of these solvents, while not problematic in many instances, may impose additional processing requirements that increase operating costs. Such efforts would not be necessary if polyceram synthesis were based on an all-aqueous (water as solvent) route. Many waste disposal and storage issues in the DOE complex could be addressed more effectively using sol-gel technology if breakthroughs in the use of water as the solvent for the sol-gel reactions were forthcoming. Finally, the use of polycerams for stabilizing salt wastes has been successfully demonstrated at the laboratory bench scale. However, development work directed towards scaling up sol-gel processing of the polyceram waste form remains to be done.



In summary, the original and primary objective for MWFA sponsorship of sol-gel development was to identify an alternative to the cement stabilization of salt-containing mixed waste. Based on the results reported in this ITSR this objective has been met. However, DOE complex wide, end user deployment of a full-scale, sol-gel stabilization technology will require the additional development outlined above. Based on response to this ITSR, it is the expectation of the MWFA that resources for this development be provided, in part, by interested end users that have direct responsibility for managing inventories of salt waste. For example, waste management personnel at Hanford's Liquid Effluent Treatment Facility are evaluating sol-gel's potential in stabilizing salt waste residues. This evaluation is based on the results of the EM-50 effort detailed in this ITSR. As a consequence they are considering advancing the technology toward deployment if an EM-50 partnership for resources can be arranged.



APPENDIX A

References

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APPENDIX B



TMS Data Elements

Funding Source

This section provides cross-reference information in regard to the EM-50 Mixed Waste Focus Area contract established for development of the sol-gel technology. The Department of Energy – Headquarters (DOE-HQ) Technology Management System (TMS) tracking number is provided as well as the specific Technical Task Plan (TTP).

TMS # 2036 Sol-Gel Stabilization of High Salt Waste

TTP # RL37MW41- Sol-Gel Stabilization of High Salt Waste



APPENDIX C

ACRONYMS

AML	Arizona Materials Laboratory
CVAA	cold vapor atomic adsorption
D&D	decontamination and decommissioning
DOE	Department of Energy
DOE-HQ	Department of Energy-Headquarters
EPA	Environmental Protection Agency
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
LI	leachability index
MLLW	mixed low-level waste
MWFA	Mixed Waste Focus Area
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NRC	Nuclear Regulatory Commission
OST	Office of Science and Technology
PBD	Polybutadiene
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
ROM	Rough-Order-of-Magnitude
SMPBD	site-modified PBD molecule
TCLP	toxicity characterization leaching procedure
TEOS	tetraethyl orthosilicate
TMS	Technology Management System
TRU	transuranic
TTP	Technical Task Plan
UTS	Universal Treatment Standard

